Energy 39 (2012) 187–195

Contents lists available at SciVerse ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Effects of pyrolysis temperature on changes in fuel characteristics of biomass char

Sang-Woo Park*, Cheol-Hyeon Jang

Department of Environmental Engineering, Hanbat National University, Daejeon 305-719, Republic of Korea

ARTICLE INFO

Article history:
Received 9 September 2011
Received in revised form
13 January 2012
Accepted 17 January 2012
Available online 21 February 2012

Keywords:
Biomass
Pyrolysis
Fuel characteristics
Combustion parameters

ABSTRACT

The fuel characteristics, the combustion profile, and the kinetic study of char that had been pyrolyzed at 300–500 °C were investigated for RH (rice husks), WC (wood chips), and WP (wood pellets). When a higher pyrolysis temperature was used, the calorific value became proportional to the fuel ratio and inversely proportional to that of the volatile matter. The pyrolysis temperature increased, the coal-band migrated toward that of coal. The number of DTG (differential thermogravimetric) peaks decreased from two to one with an increase in pyrolysis temperature. When WP was blended with coal, the unprocessed samples (WP Raw) showed two DTG peaks for all co-combustion ratios, but WP 400 (pyrolyzed at 400 °C) showed one DTG peak and a lower activation energy for all co-combustion ratios. It was observed that the combustion reaction mechanism of the WP Raw/coal-blended samples was similar to the third-order reaction model (O3) in the primary reaction (devolatilization stage), and to the diffusion model (D2–D4) in the secondary reaction (char combustion stage). On the other hand, it was thought that the secondary reaction of the WP 400/coal-blended samples had a reaction mechanism most similar to a first-order reaction (O1) at all co-combustion ratios.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Biomass is a widely used renewable energy source. With respect to the ways in which it is used, co-combustion is increasing in coal-fired power plants, which are considered a stable source of meeting demands for renewable energy sources because of the increased efficiency of energy recovery. However, a shortcoming of biomass is that its collection and transportation are costly since biomass-generating sources are widely scattered. Moreover, biomass is low in fuel value because of its high water and oxygen content. In order to address these shortcomings, torrefaction [1] has been proposed as a method of preprocessing biomass. Various studies of torrefied biomass have been carried out, focusing on mass balance [2], chemical characteristics [3,4], grindability [5,6], reactivity [5], and fuel characteristics [6–9]. Since torrefaction involves thermal treatment at 200–300 °C in a reducing atmosphere, it has a minimal impact on fuel characteristics [7,8].

Since biomass has a high percentage of volatile matter, it generally shows different combustion characteristics when it is co-combusted with coal (especially high-rank coal), for example, a significant change could be observed during the burnout time as a result of co-combustion [10–12]. Therefore, preprocessing of the biomass to minimize such changes is necessary to render fuel characteristics similar to those of coal [13]. Kastanaki and Vamvuka [14] prepared chars of olive kernels, forest residues, wood, and studied co-combustion characteristics by burning each of these materials with coal (lignite, hard coal). Their results showed an increased burnout time. Charring requires high temperatures, and this can be a drawback in terms of energy yield and cost. Sahu et al. [15] used pyrolyzed sawdust and rice husks (300 °C, 450 °C) and blended them with coal to study their fuel characteristics, but there have been few studies on the changes in fuel characteristics.

Studies are currently being conducted on gasification (or co-gasification) instead of co-combustion as a process for maximizing the efficiency of biomass energy recovery [16–18]. However, this method often raises safety issues since a large amount of tar is produced as a result of the high content of volatile matter in the biomass [19,20]. This drawback has led to studies of the gasification of biomass after enhancing its fixed carbon content by pyrolysis [21–23].

Under these circumstances, as shown in Fig. 1, the use of biomass as a material for co-combustion and co-gasification to improve energy recovery efficiency may be considered. In such a case, the fuel characteristics of the pyrolysis product (char) prepared under certain pyrolysis conditions should be evaluated.

In this study, fuel characteristics were evaluated for two types of fuels: one using the char produced under certain pyrolysis conditions, the other using a blend of char and coal. The purpose of this

---

* Corresponding author. Tel.: +82 42 821 1463; fax: +82 42 821 1476.
E-mail addresses: bigsw21@gmail.com, bigsw21@hanbat.ac.kr (S.-W. Park).

0360-5442/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.energy.2012.01.031

Nomenclature

A	pre-exponential factor, 1/min
DTG_{max}	maximum weight loss rate, %/s
E	activation energy, kJ/mol
$g(x)$	integral function of conversion
m_f	final mass of the sample
m_o	initial mass of the sample
m_t	mass of the sample at time
R_m	reactivity, %/min/K
β	heating rate, °C/min
η_E	energy yield, %
η_M	mass yield, %
BT	burnout temperature, °C
daf	dry ash free basis
db	dry basis
DTG	differential thermogravimetric
FC	fixed carbon
FR	fuel ratio
GCV	gross calorific value, kcal/kg
GCV_t	gross calorific value of pyrolysis samples
GCV_u	gross calorific value of unprocessed samples
IGCC	integrated gasification and combined cycle
IT	initial temperature, °C
OM	optimum mechanism
PT	peak temperature, °C
PW	pyrolyzed wood pellets
RH	rice husks
TG	thermogravimetric
UW	unprocessed wood pellets
VM	volatile matter
WC	wood chips
WP	wood pellets

study was to examine the effects of different pyrolysis conditions on the fuel characteristics. In this evaluation of fuel characteristics, we investigated energy yield, basic properties (ultimate analysis, proximate analysis, calorific value), fuel ratio, and coal-band using pure char samples. For the investigation of combustion profiles using TG (thermogravimetric) analysis, char samples prepared at different pyrolysis temperatures were used. The same procedure was repeated for a single type of biomass (a raw sample and char) blended with coal. For the combustion profile, DTG curves and characteristic combustion parameters were observed and a kinetic parameter was selected through the Coats–Redfern model.

2. Experimental

2.1. Preparation of samples and biomass chars

For the biomass samples, rice husks (RH), wood chips (WC), and wood pellets (WP) were selected, and the coal selected for blending was bituminous coal from the Ensham Mine (Queensland, Australia). For WC and WP (diameter : 6 mm, length : 15 mm), pitch pine (length : 10–15 mm, thickness : 5 mm) and Japanese larch (*Larix leptolepis,* bark content less than 5%), respectively, were used after natural drying. RH (length : 6 mm, width : 2 mm) that is produced in South Korea was used.

Pyrolysis was performed by placing the biomass in a hermetically sealed crucible (capacity: 25 cm^3), heating to 300, 400 and 500 °C, and then placing it in an electric furnace for 30 min to perform the pyrolysis [24]. The pyrolysis temperature was selected as the condition under which cellulose and a part of lignin were decomposed [25]. The gas from the pyrolysis was released by opening the door of the electric furnace as much as possible while maintaining the desired temperature. After pyrolysis, the air-cooled char was labeled as RH 300, RH 400 or RH 500 according to the pyrolysis temperature and biomass type (e.g., RH).

2.2. Energy yield and fuel characteristics

2.2.1. Energy yield

The mass yield (η_M) and energy yield (η_E) obtained when different temperatures and durations of pyrolysis were applied to RH, WC, and WP were determined as follows:

$$\text{Mass yield}(\eta_M) = \left(\frac{M_t}{M_o}\right)\text{dry basis} \quad (1)$$

$$\text{Energy yield}(\eta_E) = \eta_M\left(\frac{GCV_t}{GCV_U}\right)\text{dry basis} \quad (2)$$

where M_o is the mass before pyrolysis, M_t is the mass after pyrolysis, GCV_u is the gross calorific value of unprocessed samples, and GCV_t is the gross calorific value of pyrolysis samples.

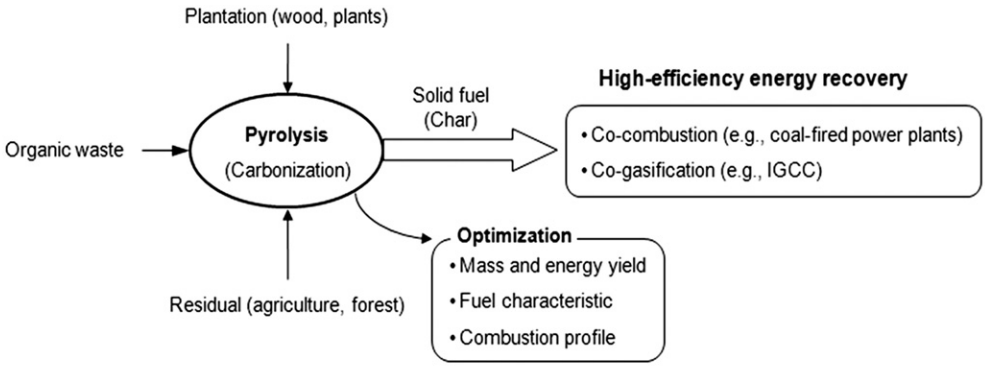
Plantation (wood, plants)
Organic waste
Pyrolysis
(Carbonization)
Residual (agriculture, forest)
Solid fuel
(Char)
High-efficiency energy recovery
• Co-combustion (e.g., coal-fired power plants)
• Co-gasification (e.g., IGCC)
Optimization
• Mass and energy yield
• Fuel characteristic
• Combustion profile

Fig. 1. Proposed pyrolysis process for various organic materials for high-efficiency energy conversion.

2.2.2. Fuel characteristics

Ultimate analysis was performed by measuring C, H, O, N, and S with an ultimate analyzer (Thermo 1112). Proximate analysis was performed in accordance with ASTM D3172, D3174, and D3175. Calorific values were measured with a calorimeter (Parr 1261 EA). Fuel ratio is a characteristic value representing the properties of a solid fuel and is indicated as a ratio (FC/VM) of VM (volatile matter) against FC (fixed carbon). The VM content was indicated on a dry, ash free (daf) basis, based on the results of the proximate analysis. The coal-band is an index which assigns a coal rank based on the degree of coalification; it was investigated using a van Krevelen diagram to plot the relationships between the atomic ratios H/C and O/C from the ultimate analysis.

2.3. TG analysis

TG analysis was conducted (TGA851e Mettler-Toledo) in an oxidation (air, 75 mL/min) atmosphere. The combustion profile was obtained by heating at a rate of 10 °C/min up to 800 °C. For thermogravimetric analysis, it is important to select the heating rate. If the heating rate is too high, the heat is not transmitted deep enough into the sample; therefore, it is desirable to select a lower heating rate [26]. For this reason, in this study, a heating rate of 10 °C/min was selected. The biomass was ground and the particles passed through a 100-mesh filter, and 10 mg sample were used.

A DTG curve, indicating rate of weight loss with increasing temperature, was prepared to determine the combustion characteristics of raw biomass, char, coal, and biomass/coal blend. On the DTG curve, the IT (initial temperature) is the temperature at which the rate of weight loss as a result of evaporation of water reaches 0.01%/s, and the PT (peak temperature) is the point where the rate of weight loss is at its maximum. The BT (burnout temperature) is the point at which the rate of weight loss decreases to 0.01%/s. The maximum rate of weight loss is indicated by $\mathrm{DTG}_{\max}$ at PT on the DTG curve [27].

From these data, reactivity can be determined as an indicator of the combustion potential of a carbonaceous material [28]. Considering that the reactivity of a fuel can be considered to be directly proportional to the maximum weight loss velocity and inversely proportional to the value of its corresponding temperature [29,30], it is interesting to introduce a parameter that is related to both properties and provides an average of the fuel reactivity. This parameter can be defined by expression (3) and represents the weight loss per temperature:

$$R_m = 100\mathrm{DTG}_{\max}\mathrm{PT}^{-1} \tag{3}$$

where, R_m is the reactivity (%/min/K), $\mathrm{DTG}_{\max}$ is the maximum weight loss rate (%/min), and PT is the peak temperature (K).

Table 1
Expressions of $g(x)$ for the kinetic model functions usually employed for solid-state reactions [12,32,33].

Mechanism	Symbol	$g(x)$
Chemical reaction		
First-order	O1	$-\ln(1-x)$
Second-order	O2	$(1-x)^{-1}$
Third-order	O3	$(1-x)^{-2}$
Limiting surface reaction between both phases		
Two dimensions	R2	$1-(1-x)^{1/2}$
Three dimensions	R3	$1-(1-x)^{1/3}$
Diffusion		
One-way transport	D1	x^2
Two-way transport	D2	$(1-x)\ln(1-x)+x$
Three-way transport	D3	$[1-(1-x)^{1/3}]^2$
Ginstling–Brounshtein equation	D4	$1-2x/3-(1-x)^{2/3}$

2.4. Kinetic parameters

The Coats–Redfern model, which was used for calculating the kinetic parameters of the co-combustion of biomass and coal by Gil et al. [12], was used in this study. The theory for the calculation of kinetic parameters by the Coats–Redfern model [31] is as follows.

A two-stage reaction kinetics scheme consisting of two independent reactions is proposed for the thermal decomposition of the

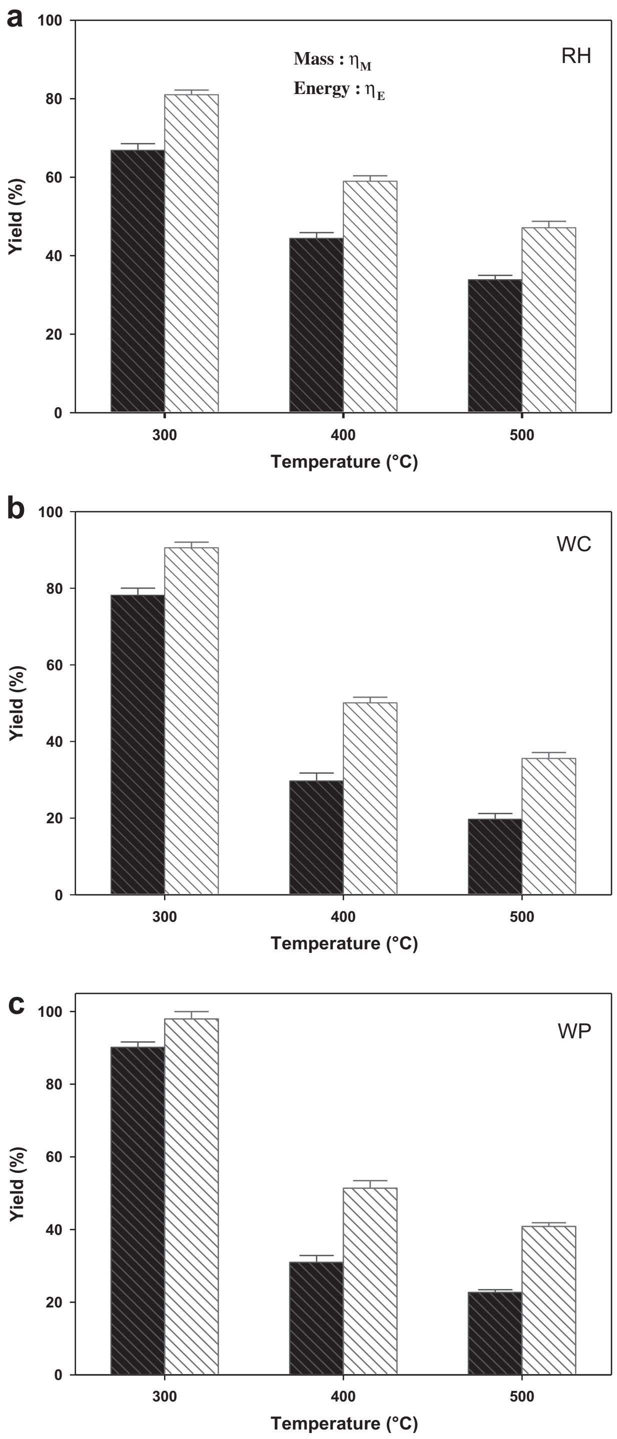

Fig. 2. Mass and energy yields for samples prepared at different pyrolysis temperatures.

biomass under an oxidative atmosphere, represented by the DTG curves. The kinetic scheme includes two separate reactions:

A (raw material) → B (intermediate) + C1 (gas) (first stage)

B (intermediate) → C2 (gas) + D (ash) (second stage)

The approach used in the present work to calculate the kinetic parameters was based on the Arrhenius equation, which has been used by other researchers to obtain the kinetic parameters of thermal events under combustion conditions.

These two separate reactions are thought to be governed by the first-order Arrhenius law, and so the kinetics of the reaction is described as:

$$\mathrm{d}x/\mathrm{d}t = kf(x) \tag{4}$$

$$k = A\exp(-E/RT) \tag{5}$$

$$x = (m_0 - m_t)/\left(m_0 - m_f\right) \tag{6}$$

where m_0 is the initial mass of the sample, m_t is the mass of the sample at time t, and m_f is the final mass of the sample.

For a constant heating rate β (°C/min) during combustion, $\beta = \mathrm{d}T/\mathrm{d}t$, Eq. (4) can be transformed into

$$\mathrm{d}x/f(x) = (k/\beta)\mathrm{d}T \tag{7}$$

Integrating Eq. (7) gives

$$g(x) = \int_0^x \mathrm{d}x/f(x) = A/\beta \int_{T_0}^{T} \exp(-E/RT)\mathrm{d}T \tag{8}$$

where $g(x)$ is the integral function of conversion.

Eq. (8) is integrated using the Coats–Redfern model, yielding

$$\ln\left[g(x)/T^2\right] = \ln[AR/\beta E(1-2RT/E)] - E/RT \tag{9}$$

Since it can be demonstrated that for most values of E and for the temperature range of combustion, the expression $\ln[AR/\beta E(1-2RT/E)]$ in Eq. (9) is essentially constant, if $\ln[g(x)/T^2]$ is plotted versus $1/T$, a straight line should be obtained. Moreover, if the correct $g(x)$ is used, the plot of $\ln[g(x)/T^2]$ against $1/T$ should give a straight line with a high correlation coefficient of linear regression analysis, from which the values of E and A can be derived. The activation energy E can be calculated from the slope of the line E/R, and by taking the temperature at which $m_\mathrm{t} = (m_0 + m_\mathrm{f})/2$ as the intercept term of Eq. (9), the pre-exponential factor A can also be calculated.

The function $g(x)$ or $f(x)$ depends on the mechanism controlling the reaction and the size and shape of the reacting particles.

Table 1 shows the expressions of $g(x)$ for the basic model functions usually employed for the kinetic study of solid-state reactions. By means of these functions, it was possible to estimate the reaction mechanisms governing the process of thermal oxidation of the samples from the TG curves. The form of $g(x)$ that gives a straight line with the highest correlation coefficient will be considered the function of the model that best represents the kinetics of mass loss for each separate reaction.

3. Results and discussion

3.1. Energy yields

As shown in Fig. 2, the mass yield and energy yield decreased as the pyrolysis temperature increased. In all samples, the energy yield was higher than the mass yield; this is mainly caused by the increased fixed carbon content as a result of discharge of volatile matter. The energy yield for each sample showed a rapid decrease in WC and WP at 400 °C because this temperature is in the range in which thermal decomposition of cellulose, a major component of wood, occurs. In contrast, a consistent decrease could be observed with RH; this is similar to the results given by Maiti et al. [34].

The mass yield was less than 50% in all samples prepared at temperatures higher than 400 °C. However, the energy yield was 50.07–58.97% for samples prepared at 400 °C and 35.57–47.12% for samples prepared at 500 °C.

3.2. Fuel characteristics

3.2.1. Basic properties

The physicochemical properties of coal, the three types of biomass, and the samples prepared at different pyrolysis temperatures are summarized in Table 2.

As shown in Table 2, the calorific value of coal is 6385 kcal/kg, which is a 1.43–1.79 time higher than the calorific values (3559–4443 kcal/kg) of the raw biomass samples. The calorific values of WC and WP, which were preprocessed by pyrolysis at 400 °C and 500 °C, respectively, were 7368–7997 kcal/kg, i.e., higher than that of coal. This is considered to be because volatile matter has been discharged during the pyrolysis process. The relationships between calorific values and VM (daf basis) and between calorific values and fuel ratios are shown in Fig. 3, and illustrate the reason for the differences in calorific values.

As shown in Fig. 3(a), the calorific values and VM have opposing trends. At 400 °C, VM decreases rapidly while the calorific value increases. However, WP 300 which was prepared at 300 °C, did not show any significant changes compared with unprocessed (Raw) samples. This is because decrease of heat transfer as the compression-molded sample and the thermal decomposition of cellulose and lignin, which is the major component of wood, not occurred at this temperature. RH samples showed relatively fewer changes than WC and WP did because its components are different from those of wood. In conclusion, we could observe that the calorific value per unit weight differed, depending on the VM content. We believe that this is characteristic of biomass which has significant oxygen and hydrogen content.

Fig. 3(b) shows the trends of changes in calorific values and fuel ratios; these trends are similar to each other. As the pyrolysis temperature increased, the fuel ratio increased. When the fuel ratio approached 1.0, the calorific value increased rapidly, but when it exceeded 1.0, the increase in the calorific value slowed down.

Table 2
Physicochemical properties of biomass chars and coal.

Sample	Proximate analysis (wt.%, db)			Ultimate analysis (wt.%, db)					GCV (kcal/kg, db)
	FC	VM	Ash	C	H	O	N	S	
Coal	58.30	29.08	12.62	74.02	4.21	6.93	1.81	0.41	6385
RH Raw	13.85	72.28	13.87	40.67	5.69	39.09	0.68	ND	3559
RH 300	15.64	64.20	20.16	46.90	4.51	27.83	0.61	ND	4314
RH 400	33.69	38.12	28.19	50.68	3.25	10.73	0.95	ND	4725
RH 500	35.36	28.41	36.23	57.40	1.87	10.21	0.49	ND	4948
WC Raw	7.71	92.24	0.05	46.73	6.46	46.35	0.41	ND	4407
WC 300	30.21	69.53	0.26	59.03	4.78	35.59	0.34	ND	5387
WC 400	64.62	35.09	0.29	72.49	4.14	22.83	0.25	ND	7430
WC 500	77.23	22.43	0.34	80.33	2.98	16.09	0.26	ND	7953
WP Raw	5.43	94.36	0.21	46.89	6.24	46.50	0.16	ND	4443
WP 300	6.53	93.13	0.34	48.60	6.21	44.68	0.17	ND	4829
WP 400	45.24	54.08	0.68	72.48	3.81	22.81	0.22	ND	7368
WP 500	80.46	18.52	1.02	81.90	3.01	13.48	0.23	ND	7997

db: dry basis, FC: fixed carbon, VM: volatile matter, GCV: gross calorific value, ND: not detected.

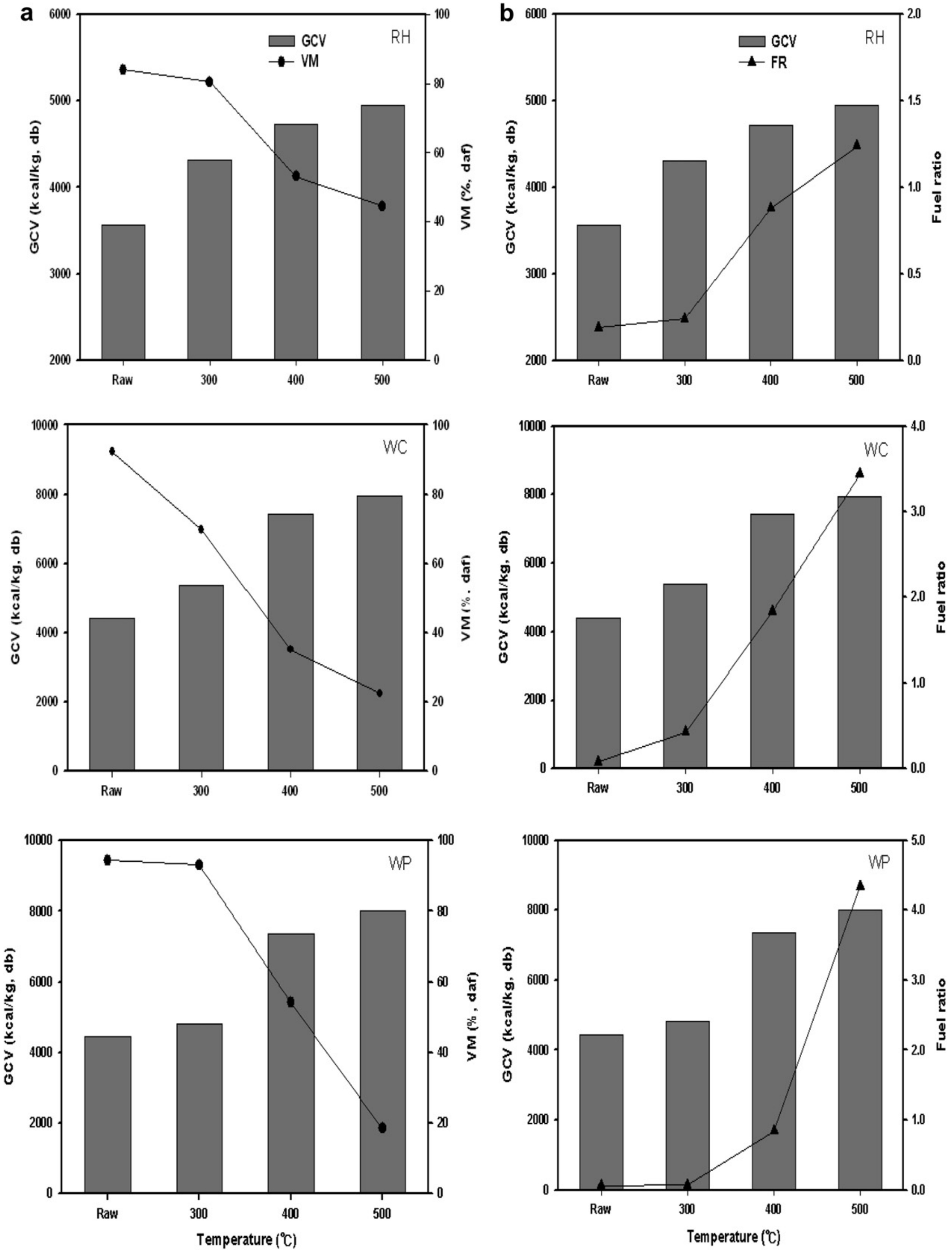

Fig. 3. Relationships between calorific values and volatile matter (a) and between calorific values and fuel ratios (b).

3.2.2. Coal-band

As shown in Fig. 4(a), it could be observed that the coal-band characteristics of the three biomass types migrated toward those of coal when the char had been prepared at higher pyrolysis temperatures because pyrolysis caused discharge of volatile matter. In contrast, Fig. 4(b), which shows the results for beech wood torrefied at 220–280 °C by Prins et al. [35], shows that a slight migration of coal-band characteristics occurred as a result of

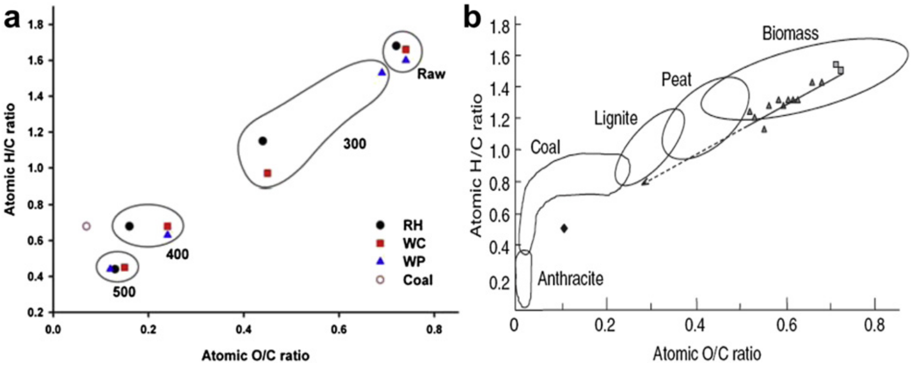

Fig. 4. Van Krevelen diagrams for samples prepared at different pyrolysis temperatures: (a) results of this study and (b) results in Prins et al. [35].

torrefaction, but the migration was still maintained within the biomass range. This means that the effect of torrefied biomass must be considered when it is used for co-combustion with coal since it does not have much different fuel characteristics.

In contrast, the biomass char prepared by pyrolysis at 300–500 °C had coal-band characteristics that were generally changed and the char was therefore not expected to show significant changes in combustion characteristics. In particular, the char

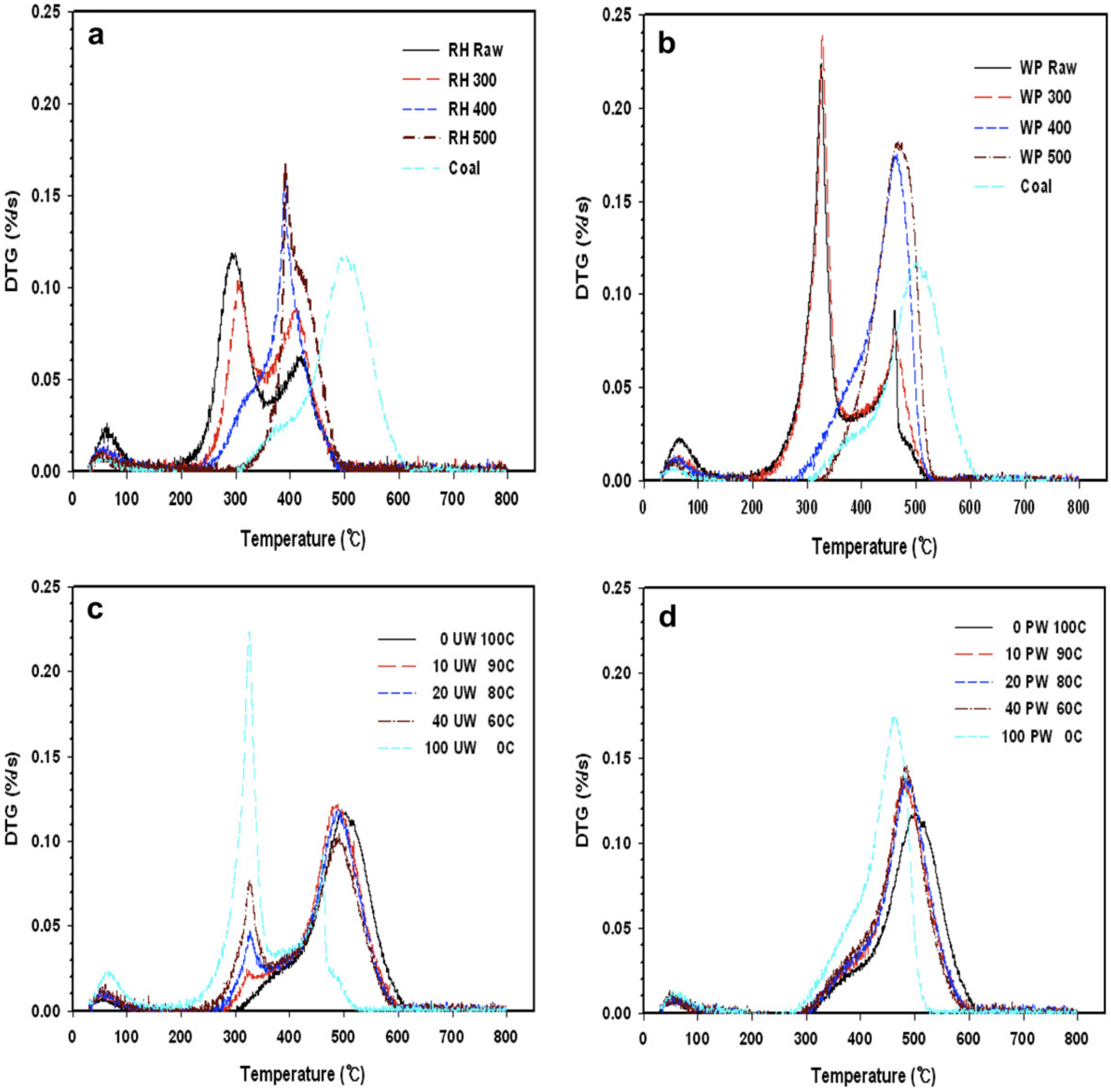

Fig. 5. DTG curves for samples.

that had been prepared at temperatures higher than 400 °C showed higher values than those of lignite, O/C 0.2–0.38 and H/C 0.8–1.3. The values of the char that had been prepared at 500 °C were O/C 0.12–0.16 and H/C 0.44 in all samples, with the H/C atomic ratio occupying an area lower than that of coal (bituminous coal).

3.3. *Combustion profiles*

3.3.1. *DTG curves*

TG analysis was performed only on RH and WP; WC was excluded because it is to WP. The DTG curves for all samples of RH and WP are shown in Figs. 5(a) and (b). The DTG curves for the blended samples of biomass (WP) and coal are shown in Figs. 5(c) and (d). Fig. 5(c) is the DTG curve of unprocessed biomass (WP Raw) and coal, and Fig. 5(d) is the DTG curve of WP 400 and coal. The co-combustion ratios of unprocessed WP Raw and coal, with WP contents of 0, 10, 20, 40, and 100% were denoted as 0UW100C, 10UW90C, 20UW80C, 40UW60C, and 100UW0C, respectively. The co-combustion ratios of WP 400 and coal, with WP contents of 0, 10, 20, 40, and 100% were denoted as 0PW100C, 10PW90C, 20PW80C, 40PW60C, and 100PW0C.

As shown in Figs. 5(a) and (b), the RH and WP samples processed by pyrolysis at 400 °C and 500 °C each had one DTG peak. However, two DTG peaks appeared for the Raw samples and the samples pyrolyzed at 300 °C. It agrees with the results obtained in a study on energy crops [36], in which two DTG peaks were observed. The samples pyrolyzed at 300 °C showed patterns similar to those of the Raw samples.

Fig. 5(c) shows two DTG peaks for the blends of unprocessed WP Raw and coal for all co-combustion ratios; the first peak is smaller at lower co-combustion ratios. Fig. 5(d) shows one DTG peak for WP 400 pyrolyzed at 400 °C for all co-combustion ratios. The shapes of the DTG peaks became similar to that of coal as the co-combustion ratio increased. The combustion parameters identified from evaluation of the DTG curves are shown in Table 3 and the combustion temperatures and weight losses for each reaction stage are shown in Table 4.

As indicated in Table 3, IT was higher in the samples preprocessed by pyrolysis than in unprocessed samples. IT increased with increasing pyrolysis at higher temperatures. However, BT did not show significant changes relative to IT. The evaluation of the combustion parameter of the blended sample of WP Raw and coal showed that IT decreased to a greater extent than BT did as the combustion ratio increased.

The co-combustion of WP Raw and coal showed that the burnout time increased as the co-combustion ratio increased. However, a study [37] using blended samples of three types of lignite and biomass (wood) reported that the burnout time decreased as the co-combustion ratio increased; this is believed to be because the types of coal used for blending were lignite and bituminous coal. In other words, it is because bituminous coal contains less volatile matter than biomass and lignite contain.

In contrast, the blended samples of WP pyrolyzed at 400 °C (WP 400) and coal showed decreased burnout times. Kastanaki and Vamvuka [14] reported that the burnout time of char pyrolyzed at 850 °C was shorter than that of coal (lignite, hard coal). However, they also reported that the burnout time tended to increase when the char was co-combusted with coal; this is contrary to the results of our study. From these results, it can be concluded that different chemical and physical characteristics of the biomass char can be obtained by applying different pyrolysis temperatures.

The reactivities of WP Raw, WP 400, and coal were 2.239, 1.426, and 0.905, respectively, showing that WP Raw had the highest value among the unblended components. However, the reactivity of the blended samples of WP Raw and coal showed opposite results. The reactivity of the blend decreased as the co-combustion ratio of WP Raw increased, although WP Raw has the highest reactivity. This result is contradictory to the reactivity results for blended samples (grape pomace and Pyrenean oak pellets) reported by Miranda et al. [29]. However, the reactivity of the blended sample of WP 400 and coal showed increased reactivity. The blending of biomass with bituminous coal instead of lignite seems to reduce the increase in reactivity; this can also be observed in terms of the burnout time.

As shown in Table 4, the weight loss of RH Raw was greater in the first reaction (50.44%) than in the second reaction (29.13%). The weight loss rate was higher in the first reaction for both WP Raw and WP 300. It is considered that the reason was because the thermal decomposition of wood components did not occur at 300 °C, as mentioned above with regard to fuel characteristics. In contrast, the weight loss of the blended sample of WP Raw and coal showed a gradual increase as the co-combustion ratio increased in the first reaction stage.

Table 3
Combustion parameters obtained from DTG combustion profiles for coal, biomass char, and biomass/coal blends.

Sample		IT (°C)	PT (°C)		DTG_{max} (%/S)		BT (°C)	t_q (min)	Reactivity (%/min/K)
			PT1	PT2	DTG1	DTG2			
Coal		337	–	501	–	0.1168	598	26.1	0.905
Biomass	RH Raw	228	299	421	0.1188	0.0620	474	24.6	1.246
	300	254	306	412	0.1028	0.0889	476	22.2	1.065
	400	273	–	389	–	0.1599	474	20.1	1.449
	500	343	–	392	–	0.1679	484	14.1	1.515
	WP Raw	243	326	460	0.2235	0.0910	504	26.1	2.239
	300	251	328	461	0.2383	0.0793	510	25.9	2.379
	400	306	–	464	–	0.1752	514	20.8	1.426
	500	347	–	468	–	0.1814	525	17.8	1.469
Biomass (WP Raw) + Coal	0UW100C	337	–	501	–	0.1168	598	26.1	0.905
	10UW90C	305	320	489	0.0246	0.1220	585	28.0	0.961
	20UW80C	290	328	491	0.0461	0.1182	576	28.6	0.928
	40UW60C	278	327	490	0.0765	0.1046	573	29.5	0.823
	100UW0C	243	326	460	0.2235	0.0910	504	26.1	2.239
Biomass (WP 400) + Coal	0 PW100C	337	–	501	–	0.1168	598	26.1	0.905
	10 PW90C	329	–	475	–	0.1336	581	25.2	1.072
	20 PW80C	327	–	488	–	0.1383	578	25.1	1.090
	40 PW60C	323	–	486	–	0.1453	571	24.8	1.149
	100PW0C	306	–	464	–	0.1752	514	20.8	1.426

t_q: burnout time (BT-IT).

Table 4
Temperature intervals for different regions after loss of moisture, mass loss in these regions, and residues for all samples.

Sample		Temperature interval (°C)		Weight loss (%)		
		Reaction 1	Reaction 2	Reaction 1	Reaction 2	Residue (%)
Coal		–	337–598	–	85.48	12.19
Biomass	RH Raw	228–359	359–474	50.44	29.13	11.02
	300	254–353	353–476	34.54	41.54	17.85
	400	–	273–474	–	66.67	26.12
	500	–	343–484	–	57.76	37.11
	WP Raw	243–370	370–504	57.58	32.84	0.05
	300	251–377	377–510	58.69	35.05	0.13
	400	–	306–514	–	95.59	0.26
	500	–	347–525	–	97.11	0.39
Biomass (WP Raw) + Coal	0UW100C	–	337–598	–	85.48	12.19
	10UW90C	305–352	352–585	2.94	85.39	10.10
	20UW80C	290–356	356–576	3.45	86.34	9.02
	40UW60C	278–365	365–573	5.35	85	7.42
	100UW0C	243–370	370–504	57.58	32.84	0.05
Biomass (WP 400) + Coal	0 PW100C	–	337–598	–	85.48	12.19
	10 PW90C	–	329–581	–	83.75	10.30
	20 PW80C	–	327–578	–	81.67	8.54
	40 PW60C	–	323–571	–	89.10	7.54
	100PW0C	–	306–514	–	95.59	0.26

3.3.2. *Kinetic parameters*

As shown by the DTG curve (Fig. 5), the single-reaction conditions are the co-combustion of coal and biomass pyrolyzed at 400 °C and 500 °C and the co-combustion of WP 400 and coal. Other conditions involve two reactions, which need to be examined for each reaction-rate factor.

As shown in Table 5, the optimum mechanisms for the first reaction and the second reaction for all samples differed from each other. However, the D3 mechanism was found to be the best when 20–40% of RH Raw, RH 300, or WP Raw was blended with coal in the first reaction stage. In contrast, the second reaction of the blended sample of WP 400 and coal showed O1 (first reaction) to be the best mechanism for all co-combustion ratios. However, in the case of coal, the O1 (1st order chemical reaction) mechanism showed the highest correlation coefficient (R^2), 0.9597. The activation energy differed for each sample and for each pyrolysis temperature, as well as between the first and the second reactions. The activation energy (E) of the unprocessed sample was shown to be in the range 100.31–103.96 kJ/mol in the 1st stage and 19.57–49.44 kJ/mol in the 2nd stage. Compared with 122.6 kJ/mol and 15.3 kJ/mol, which were the results obtained by Yorulmaz and Atimatay [32], and 119 kJ/mol and 145 kJ/mol, which were the results obtained by Shen et al. [38], the 1st stage showed lower values and the 2nd showed intermediate values.

For the samples that involved first and second reactions, the greater activation energy was shown during the first reaction. Also, an increased activation energy could be observed in both the first and the second reactions at higher pyrolysis temperatures. WP 500 pyrolyzed at 500 °C had an activation energy of 227.18 kJ/mol, which was higher than the value of 145.3 kJ/mol for wood char thermally treated at 850 °C [14]. When WP Raw and coal were blended at a ratio of 10–40%, the activation energy decreased when the co-combustion ratio was lower, in both the first and the second reactions. However, this change was not greater than the change observed with the blended sample of WP 400 and coal.

Although the activation energy of WP 400 was 136.74 kJ/mol, which was higher than the value of 108.35 kJ/mol for coal, the activation energy of its co-combustion decreased to 74.97 kJ/mol for a 10% co-combustion ratio, and to 69.08 kJ/mol for a 40% co-combustion ratio. The activation energy was generally greater as

Table 5
Thermal kinetic results of all samples.

Sample		Reaction 1				Reaction 2			
		OM	E (kJ/mol)	A (1/min)	R^2	OM	E (kJ/mol)	A (1/min)	R^2
Coal		–	–	–	–	O1	108.35	$3.8E+07$	0.9597
Biomass	RH Raw	D3	103.96	$6.9E+07$	0.9783	D3	49.44	$6.1E+02$	0.9888
	300	D3	139.26	$3.4E+10$	0.9833	O3	79.99	$1.3E+07$	0.9823
	400	–	–	–	–	D3	104.70	$6.5E+06$	0.9865
	500	–	–	–	–	O3	118.23	$9.3E+04$	0.9607
	WP Raw	D1	100.31	1.3E + 08	0.9718	R2	19.57	$5.0E+00$	0.9731
	300	D3	145.92	1.9E + 11	0.9775	D1	30.00	$4.9E+01$	0.9879
	400	–	–	–	–	D2	136.74	$3.2E+09$	0.9979
	500	–	–	–	–	D3	227.18	$2.3E+15$	0.9987
Biomass (WP Raw) + Coal	0W100C	–	–	–	–	O1	108.35	$3.8E+07$	0.9597
	10W90C	O3	7.41	$5.8E-01$	0.9938	D3	126.56	$4.0E+07$	0.9884
	20W80C	D3	152.40	$3.4E+10$	0.9909	D4	96.95	$3.1E+05$	0.9840
	40W60C	D3	134.25	$2.4E+09$	0.9838	D2	73.83	$3.4E+04$	0.9838
	100W0C	D1	100.31	$1.3E+08$	0.9718	R2	19.57	$5.0E+00$	0.9731
Biomass (WP 400) + Coal	0W100C	–	–	–	–	O1	108.35	$3.8E+07$	0.9597
	10W90C	–	–	–	–	O1	74.97	$1.5E+04$	0.9910
	20W80C	–	–	–	–	O1	72.39	$9.7E+03$	0.9919
	40W60C	–	–	–	–	O1	69.08	$6.2E+03$	0.9901
	100W0C	–	–	–	–	D2	136.74	$3.2E+09$	0.9979

OM : Optimum mechanism, E: Activation energy, A: pre-exponential factor.

the co-combustion ratio increased, but these results showed decreasing activation energies. This is a trend similar to the reactivity trend shown in Table 3; this is considered to be the result of the chemical and physical changes caused by pyrolysis increasing combustibility. Okumura et al. [23] studied the effects of the pyrolysis conditions of biomass on gasification reactivity. In their report, they suggested that application of appropriate temperature conditions is important because the atomic bonds of carbon become stronger, reducing the reactivity when the pyrolysis temperature is higher.

4. Conclusions

The results of the study on the effect of pyrolysis temperature on fuel characteristics of biomass are as follows. It was observed that, as the pyrolysis temperature increased, the energy yield decreased and the coal-band migrated toward that of coal. The calorific value of char changed depending on the VM content and showed a higher value when the fuel ratio approached 1.0. An investigation of the combustion parameters showed that the burnout time decreased and the reactivity increased as the pyrolysis temperature increased. When the raw samples were blended with coal, the burnout times of the samples increased, and the reactivity decreased, but the samples pyrolyzed at 400 °C showed the opposite trend, indicating that the fuel characteristics had been changed. The activation energy differed for each sample and at each pyrolysis temperature, as well as between the first and second reactions. The combustion reaction mechanism for WP 400 blended with coal showed only a primary chemical reaction (O1) at all co-combustion ratios, but the unprocessed sample (WP Raw) showed different results, depending on the primary and secondary reactions. As a result, it could be shown that the fuel characteristics of the pyrolyzed samples were approaching those of coal, as compared to the fuel characteristics of the unprocessed sample. Based on this result, it is thought that further study on the optimization of the pyrolysis temperature to ensure economic feasibility is warranted and should be performed in future.

References

[1] Bergman PCA, Boersma AR, Zwart RWR, Kiel JHA. Torrefaction for biomass co-firing in existing coal-fired power stations "BIOCOAL". Energy Research Centre of the Netherlands (ECN); 2005.
[2] Prins MJ, Ptasinski KJ, Janssen FJJG. Torrefaction of wood. part 1. weight loss kinetics. J Anal Appl Pyrol 2006;77(1):28–34.
[3] Prins MJ, Ptasinski KJ, Janssen FJJG. Torrefaction of wood. part 2. analysis of products. J Anal Appl Pyrol 2006;77(1):35–40.
[4] Pentananunt R, Rahman MANM, Bhattacharya SC. Upgrading of biomass by means of torrefaction. Energy 1990;15(12):1175–9.
[5] Arias B, Pevida C, Fermoso J, Plaza MG, Rubiera F, Pis JJ. Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Process Technol 2008;89(2):169–75.
[6] Phanphanich M, Mani S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. Bioresour Technol 2011;102(2):1246–53.
[7] Bridgeman TG, Jones JM, Shield I, Williams PT. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel 2008;87(6):844–56.
[8] Rousset P, Aguiar C, Labbe N, Commandre JM. Enhancing the combustible properties of bamboo by torrefaction. Bioresour Technol 2011;102(17):8225–31.
[9] Almeida G, Brito JO, Perre P. Alterations in energy properties of eucalyptus wood and bark subjected to torrefaction: the potential of mass loss as a synthetic indicator. Bioresour Technol 2010;101(24):9778–84.
[10] Biaginia E, Cionib M, Tognotti L. Development and characterization of a lab-scale entrained flow reactor for testing biomass fuels. Fuel 2005;84(12–13):1524–34.
[11] Gurgel VCA, Saastamoinen J, Carvalho Jr JA, Aho M. Over lapping of the devolatilization and char combustion stages in the burning of solid fuel particles. Combust Flame 1999;116(4):567–79.
[12] Gil MV, Casal D, Pevida C, Pis JJ, Rubiera F. Thermal behaviour and kinetics of coal/biomass blends during co-combustion. Bioresour Technol 2010;101(14):5601–8.
[13] Maciejewska A, Veringa H, Sanders J, Peteves SD. Co-firing of biomass with coal: constraints and role of biomass pre-treatment. EUR 22461 EN; 2006.
[14] Kastanaki E, Vamvuka D. A comparative reactivity and kinetic study on the combustion of coal-biomass char blends. Fuel 2006;85(9):1186–93.
[15] Sahu SG, Sarkar P, Chakraborty N, Adak AK. Thermogravimetric assessment of combustion characteristics of blends of a coal with different biomass chars. Fuel Process Technol 2010;91(3):369–78.
[16] McKendry P. Energy production from biomass (part 3): gasification technologies. Bioresour Technol 2002;83(1):55–63.
[17] Valero A, Usón S. Oxy-co-gasification of coal and biomass in an integrated gasification combined cycle (IGCC) power plant. Energy 2006;31(10–11):1643–55.
[18] Ptasinski KJ, Prins MJ, Pierik A. Exergetic evaluation of biomass gasification. Energy 2007;32(4):568–74.
[19] Han J, Kim HJ. The reduction and control technology of tar during biomass gasification/pyrolysis: an overview. Renew Sust Energ Rev 2008;12(2):397–416.
[20] Bhattacharya SC, Mizanur R, Siddique AHM, Pham HL. A study on wood gasification for low-tar gas production. Energy 1999;24(4):285–96.
[21] Ahmed II , Gupta AK. Kinetics of woodchips char gasification with steam and carbon dioxide. Appl Energy 2011;88(5):1613–9.
[22] Khalil R, Vrhegyi G, Jschke S, Grønli MG, Hustad J. CO_2 gasification of biomass chars: a kinetic study. Energy Fuels 2009;23(1):94–100.
[23] Okumura Y, Hanaokab T, Sakanishi K. Effect of pyrolysis conditions on gasification reactivity of woody biomass-derived char. In: Proceedings of the combustion institute, vol. 32; 2009. p. 2013–20 (2).
[24] Yuan JH, Xu RK, Zhang H. The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresour Technol 2011;102(3):3488–97.
[25] Sjöström E. Wood chemistry: fundamentals and applications. 2nd ed. San Diego: Academic Press; 1993.
[26] Vamvuka D, Sfakiotakis S. Combustion behaviour of biomass fuels and their blends with lignite. Thermochim Acta 2011;526(1–2):192–9.
[27] Biswas S, Choudhury N, Sarkar P, Mukherjee A, Sahu SG, Boral P, et al. Studies on the combustion behaviour of blends of indian coals by tga and drop tube furnace. Fuel Process Technol 2006;87(3):191–9.
[28] Russell N, Beeley T, Man C, Giggins J, Williamson J. Development of TG measurements of intrinsic char combustion reactivity for industrial and research purposes. Fuel Process Technol 1998;57(2):113–30.
[29] Miranda MT, Arranz JI, Román S, Rojas S, Montero I, López M, et al. Characterization of grape pomace and pyrenean oak pellets. Fuel Process Technol 2011;92(2):278–83.
[30] Ghetti P, Ricca L, Angelini L. Thermal analysis of biomass and corresponding pyrolysis products. Fuel 1996;75(5):565–73.
[31] Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. Nature 1964;201(1):68–9.
[32] Yorulmaz SY, Atimtay AT. Investigation of combustion kinetics of treated and untreated waste wood samples with thermogravimetric analysis. Fuel Process Technol 2009;90(7–8):939–46.
[33] Guo J, Lua AC. Kinetic study on pyrolytic process of oil-palm solid waste using two-step consecutive reaction mechanism. Biomass Bioenergy 2001;20(3):223–33.
[34] Maiti S, Dey S, Purakayastha S, Ghosh B. Physical and thermochemical characterization of rice husk char as a potential biomass energy source. Bioresour Technol 2006;97(16):2065–70.
[35] Prins MJ, Ptasinski KJ, Janssen FJJG. More efficient biomass gasification via torrefaction. Energy 2006;31(15):3458–70.
[36] Jeguirim M, Dorge S, Trouvé G. Thermogravimetric analysis and emission characteristics of two energy crops in air atmosphere: Arundo donax and Miscanthus giganthus. Bioresour Technol 2010;101(2):788–93.
[37] Varol M, Atimtay AT, Bay B, Olgun H. Investigation of co-combustion characteristics of low quality lignite coals and biomass with thermogravimetric analysis. Thermochim Acta 2010;510(1–2):195–201.
[38] Shen DK, Gu S, Luo KH, Bridgwater AV, Fang MX. Kinetic study on thermal decomposition of woods in oxidative environment. Fuel 2009;88(6):1024–30.